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Procedia Materials Science 5 (2014) 648 – 655
Procedia Materials Science
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International Conference on Advances in Manufacturing and Materials Engineering, AMME 2014

Dry sliding wear behavior of SiC reinforced Titania coating deposited by High Velocity Oxy Fuel spraying

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Abstract

The Conventional Titania (TiO_2) and Titania blends with 10% SiC powder was thermally sprayed on commercially pure titanium substrate using High Velocity Oxy-Fuel (HVOF) spraying. The microhardness value of these coatings was measured by Vickers microhardness tester. The coating porosity, cross sectional morphology and wear surface morphologies was observed in Optical Micrograph (OM) and Scanning Electron Micrograph (SEM). The X-Ray Diffraction analysis was made to observe the phase composition of these coatings. The wear behavior of these coatings was studied in Pin-on-Disk arrangement as per ASTM G99 standard. It was found that addition of SiC enhances the hardness and wear resistance of the coating. Further, wear surface morphology was analysed and possible wear mechanisms were discussed.

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Keywords: *HVOF spraying,Titania(TiO_2), Dry sliding wear,microhardness*Introduction

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doi:10.1016/j.mspro.2014.07.311

1. Introduction

Titanium and Titanium alloys posses several excellent properties including corrosion resistance, very high strength to weight ratio, low density and ability to maintain their properties at extremely high temperatures. These attractive properties of Titanium and its alloys makes them suitable for wide applications ranging from aerospace, chemical, petrochemical, marine and offshore. On the other hand, titanium alloys are limited its applications because of its poor tribological properties and galling properties, this is due to low resistance to plastic shearing as well as low protection by surface oxide film formed as a consequence of high flash temperature (induced by frictional heating) during sliding makes unstable friction coefficients, severe adhesive wear, susceptibility to fretting wear, and a strong tendency to seize (Yetim,2010; Chan Huang et al,v 2012). Gicouel.A et al (1990) and Toshiro Kotaki (1998) reported many surface treatments (like low-dose-rate implantation, ion beam deposition, plasma nitration and carburization) have been used to modify the tribological properties of titanium and titanium alloys, among those techniques thermal sprayed ceramic coatings alumina, chromia, zirconia and Titania offers higher wear, erosion and corrosion resistance. Thermal sprayed Titania (TiO_2) has very good corrosion resistance, biocompatible and also TiO_2 gives moderate wear resistance while it employed in hard surfaces (sliding wear) and abrasive grains due to its high hardness, density, and adhesion strength. TiO_2 under goes plastic smearing under lubricated contact and shows considerable wear resistance in dry sliding (Dai.W.W et al, 1996; Lima.R.S et al, 2008). It was reported that microstructure and bond strength of the thermal sprayed Titania coating on titanium components is superior to other ceramic coatings due to its better Coefficient of thermal expansion (CTE) match with titanium substrate. G.E. Kim et al (2007) studied about dry abrasive and slurry erosive wear behavior of plasma sprayed nano structured titania on titanium substrate , he suggested that addition of titania with second phase ultrafine particle selected from the group consist of zirconia, tantalum oxide, boron carbide, Silicon Carbide(SiC), titanium carbide can improve the wear resistance. In this investigation first attempt has been made to develop Titania (TiO_2) with 10%SiC by High Velocity Oxy-Fuel (HVOF) and its wear behavior has been studied in Pin-on-disk apparatus.

2. EXPERIMENTAL WORK

2.1. Thermal spraying

The fused and crushed TiO_2 and SiC powders with size ranging between 10-30μm (H.C Stark, AMPERIT , supplied by M/S Metallizing Equipment Co. Pvt. Ltd., Jodhpur, India) was used. The powder was prepared by mechanically mixing TiO_2 with 10% volume of SiC by high energy ball milling machine using a jar with tungsten carbide balls. Ball milling was carried out for one hour with ball to weight ratio 1:1, filling 25% of jar volume at the speed of 150 rpm. The Titanium (composition of titanium is shown in table-1) substrate (Ø 40 mm X 3 mm thickness) was grit blasted by using corundum grits of size 320- 500μm and subsequently cleaned using acetone in an ultrasonic bath and dried. The HVOF spraying was carried out using equipment supplied by M/S Metallizing Equipment Co. Pvt. Ltd., Jodhpur, India, which utilizes the supersonic jet generated by the combustion of liquid petroleum gas (LPG) and oxygen mixture. LPG fuel gas is cheap and readily available as compared to other fuels used for HVOF spraying. The spraying parameters employed during HVOF deposition are listed in Table-2. All the process parameters, including the spray distance were kept constant throughout the coating process.

2.2 Coating characterization

The average thickness of the coating is 200-250 μm, the cross sectional morphology has been observed in optical micrograph. Standard metallographic procedures were adopted to polish the cross section of the coating. The porosity of the coatings was analysed as per ASTM B276 standard on the polished cross-section of the coating, using optical microscope (OM) (Make: Meiji; Japan, Model: MIL-7100) equipped with image analysing system. Customary metallographic procedures were adopted to polish the cross-section of the coatings. A 200 μm square area was selected on the polished cross-section of the coating, and the image was analysed. The same procedure was repeated at five random locations to find out the average percentage volume of porosity. The microhardness measurement was made using a Vickers Microhardness tester (Make: Shimadzu; Japan. Model: HMV-2T). A load of 300 g and a dwell time of 15 s were used to evaluate the hardness. Hardness values were measured at 10 random locations on the polished cross-section of a coating. A phase composition of as sprayed coating was characterized by X-ray diffraction(XRD) analysis using Cu Kα radiation at a moderate scanning speed of 1° per minute between 2θ=20-80°. Optical microscope (OM) was used to investigate the microstructural characterization of uncoated titanium surface and coated titanium surfaces.

Table 1. Chemical composition of Titanium

Al	Sn	Fe	Cr	V	Ti
0.0035	0.0195	0.04425	0.00287	0.03737	Remaining

Table 2. HVOF Spray parameters

Oxygen flow rate	262 l/min
Air-flow rate	700 l/min
Fuel (LPG) flow rate	72 l/min
Spray distance	220 mm
Powder feed rate	33 g/min

2.3 Dry sliding wear test

Wear tests were carried out in a wear testing machine (Make: DUCOM; India. Model: TR-20-PHM-M1) with a Pin-on-disc configuration under dry sliding conditions as per ASTM G99-04 without eliminating the debris formed during sliding. The Ø40 mm uncoated titanium and TiO_2, TiO_2+10%SiC coated specimens are pressed on rotating wear disc acted as counter surface against WC (hardness 1470 $HV_{0.5}$) pin with normal load 30N. The radius of the travelling circle of pin was 2cm. The total sliding distance and sliding speed was 500m, 300 rpm respectively. The loss of material was measured before and after the test by means of a precision weighing machine with 0.01mg of resolution. At least two samples were tested at each experimental condition to ensure reliability of results. In order to explicate the wear process and wear mechanism, the worn surfaces and wear debris were examined by scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) and OM respectively.

3. RESULTS AND DISCUSSION

3.1 Microstructure, hardness and porosity of the coating

The fig-1(a) shows the SEM morphology of fused and crushed TiO_2 feedstock. It exhibits angular, blocky morphology of dense solid particles and absence of nanostructural characteristics, which confirms the conventional character of feedstock. Fig-1(b) shows the submicron size SiC which consist narrow particle distribution. Fig-2 shows the Optical Micrograph images of coating cross section by HVOF, all the coating exhibits the uniform microstructure such as absence of lamellar structure even distribution of pores and no significant micro crack. The coating shows porosity level in between 1-2%. It is thought that high impact velocity of the sprayed particle is one of the main factors producing low porosity, highly dense and homogeneous coating. This result is well agreed with previous studies on HVOF sprayed TiO_2 coating and this will exhibit near isotropic behavior in mechanical properties (Lima.R.S, 2004). The Vickers micro hardens numbers (300g at 15 s) for the titanium surface measured at the top surface of the titanium is 207 $HV_{0.3}$. The values measured at cross section of TiO_2 and TiO_2+10%SiC coated surfaces are 876 and 958 $HV_{0.3}$ respectively. The addition of SiC into the TiO_2 coating matrix increases the coating hardness and decreases the coating porosity. The SiC feedstock employed in this study has narrow particle size, high specific surface area and high chemical activity leads to agglomeration with melted Titania particles which give strong cohesion between the splats and subsequently decreasing porosity, so the increasing microhardness was observed. The higher hardness and other mechanical properties are limited by degree of contact between splats or between splat and substrate. The higher particle velocity of HVOF spraying may improve the true contact area thereby increasing the hardness of the coating (Yandouzi M et al, 2009).

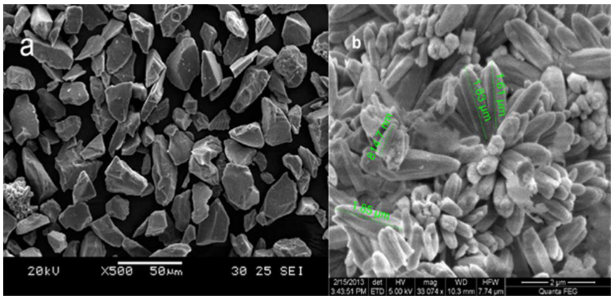

Fig-1 SEM Morphology of Feed stock (a) TiO_2 (b) SiC

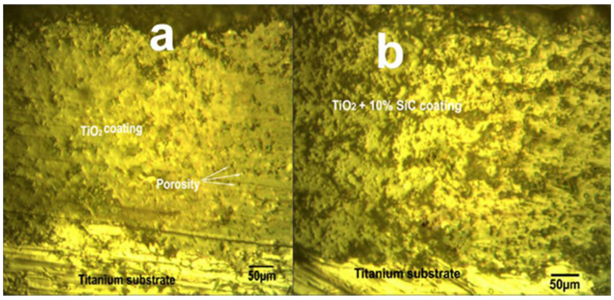

Fig-2 Optical Micrograph of coating cross section (a) TiO_2 coating (b) TiO_2 + 10%SiC

3.2 Crystallographic phases

Fig. 3(a) shows the XRD pattern of the Titania coating contained rutile as a major phase and anatase minor phase. No significant degradation of Titania phases was observed, it means coating consist stoichiometric Titania phases. The crystalline phases of SiC were evidenced from the XRD pattern shown in fig-3(b), the intensity of SiC peak increases while increasing percentage of SiC. It also evidenced that there is TiC and SiO_2 second phase exist in the XRD pattern, we could understand that there is chemical reaction takes place during thermal spraying. It may be due to inherent nature of SiC which undergoes decomposition at high temperature during HVOF spraying (Seyed Hashem Alavi, 2012).

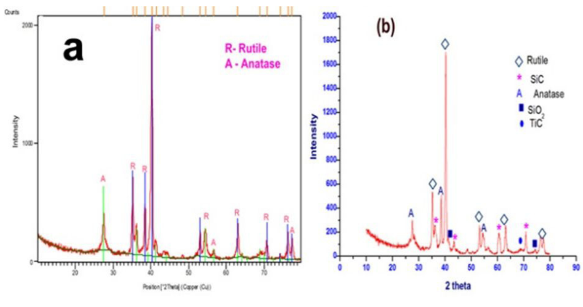

Fig-3 XRD pattern of (a) TiO_2 Coating (b) TiO_2+10% SiC

3.3 Tribological performance

Fig-4(a-b) shows the wear rate and coefficient of friction of the titanium substrate and coated titanium, from the graph it is clear that the pure titanium has much higher wear rate than coated titanium. The friction coefficient result shows the titanium has higher coefficient of friction (0.3-0.5) than other three coated surfaces. Initially when the pin loaded on titanium the contact pressure between sliding ball and substrate was high, so the initial break up of asperities taking place, the wear debris generated from the wear surfaces during this running in period becomes the case of three body abrasion rather than two body sliding. This is the main reason for increase in coefficient of friction (Ramachandran.C.S, 2012). It should be explained through the wear morphology of Titanium substrate (fig 5a), the SEM image of worn surface presented vestige with plastic deformation and delamination as well as ridges along sliding direction through continuous squashing and smearing by the counterface. Rigney proposed by the experimental observations that the sliding of metals can be described by the following wear sequence: surface and sub surface plastic deformation, formation of wear debris and material transfer, reaction with the environment, mechanical mixing and formation of tribo-layer (Rigney.D.A, 1992). At present investigation, during sliding of Titanium, tribolayer supposed to be formed through metal debris being produced or transferred, ground, mixed, compacted and even sintered on worn surfaces. In this procedure metal debris would react with oxygen. The tribolayer formation is depends the sliding condition (sliding velocity, load and sliding distance), sliding material and counterface material used (Hsu.S.M et al, 1997). Fig-5(a) shows the SEM morphology of the Titanium worn surface which confirms the presence of tribolayer, the surface layer supposed to be mechanically mixed layer (MML). Fig 5(b) shows the Electron Dispersive Spectroscopy (EDS) analysis confirms that main element is Ti and some minor amount of oxygen and tungsten (W) elements. Oxygen presence is due to reaction with atmosphere and presence of tungsten (W) definitely from material transfer from tungsten carbide (WC) pin used in this study.

The mechanism of wear in titanium is oxidative wear and adhesive wear, the uncoated Titanium shows very high wear rate which may be associated with the preferential transfer of titanium to WC counterface, this was typical adhesive wear. Dong and Bell (2000) reported that Titanium is chemically active and have a high ductility which gives rise to the strong tendency to adhesion which is well suited with this study. The transferred Titanium film becomes work hardened after multiple contacts in the wear couple which in turn results in severe abrasive wear damage to the titanium surface.

Fig 6 (a) shows the SEM morphology of wear surface of TiO_2 coating, the surface exhibited rough layer of plastically deformed surface caused by brittle fracture, spallation, delamination and minor plastic deformation under sliding wear. Observation of worn surface indicated presence of debris on worn surface, the EDS analysis shows (fig 6b) fragmented debris and the layer consist TiO_2 particles, the presence of WC is not evidenced. It has been noticed that wear scares of these type already reported in previous work (Miyayama.M et al, 1991). Plastic deformation and fragmentation occur during the wear of ceramic materials, in wear of ceramic material a transition of material removal mechanism from ductile mode to brittle mode occurs. The initial ductile flow progressively changes to brittle fracture after critical depth of cut is reached. In the as deposited coatings, brittle fracture occurs from the very beginning of the test, probably because of the very high pressure on the few surface asperities bearing whole contact load, so friction coefficient is high shown in fig-4b.

The wear resistance of coating containing 10%SiC was significantly higher when compared to TiO_2 coating. Fig 7(a) shows the SEM morphology of worn surface of 10% SiC addition coating, it appears to be smooth without many grooves. The wear track shows less wear mode, where plastic deformation and surface polishing are the preferred wear mechanism. We could see the well adhered tribofilm on the worn surface which is formed by strongly deformed wear debris generated during continuous sliding, the debris generation may be very slow and sizes of the wear debris are very small and possess high surface energy which leads to formation of lumps. They accumulate in wear track and adhere to the surface. These fine particles disperse between the ceramic coating and counterface and act as a bearing agent which can not only bear the applied load but also prevents direct contact results in a decrease in friction coefficient and wear rate. It is well understood that this 10% SiC coating has the capability to form smooth and compact tribofilm by local plastic deformation is the key property determining coating performance in sliding wear. Xie and Hawthorne (2006) have shown that under sufficiently high hydrostatic pressures, brittle ceramic materials may be prevented from cracking so that any permanent deformation is essentially plastic. Therefore, the localised compression force acting on the ceramic coated pin, aided by high local temperature generated during wear testing, may be high enough to prevent brittle failure, thereby allowing plastic deformation and the formation of smooth wear tracks.

The tribofilm formation on the worn surface has been evidenced through EDS results (fig-7b) shows the presence of Si, O and Ti on the worn surface. The tribofilm formed in this coating is fragmented during repeated sliding and removed as wear debris. Addition of SiC increases wear resistance compared to TiO_2 coating which delays the wear transition from severe wear to mild wear. However, mild wear in which the only roughening of the surface was associated with differential wear between grains (Belmonte.M et al, 2006). Since the wear is caused by crack initiation and crack growth along the grain boundary, after combination of several cracks, which initiate at different depths, the combined cracks propagate at the depth of orthogonal shear stress and eventually reach the surface and cause localized spallation of splats. SiC particles present in the matrix reduce the crack propagation and act as crack arrester in the coating (Adachi.K et al, 1997).

3.4 Wear debris analysis

The accumulation of wear debris during sliding is obviously a major factor affecting the wear behavior of both substrate and coating. Since it can induce accelerated wear rates by changing what is essentially a two body sliding system into three body abrasion. OM observation of wear debris generated by sliding uncoated Titanium against WC shows (fig-8a) debris in the form of flakes, the nature of the flaky debris reveals sliding marks which due to the compaction of debris during continuous sliding of ball repeatedly traversing across the accumulated debris (Fernlindez JE et al ,1996). Wear debris collected during sliding of TiO_2 coating show in fig-8b, which has fine debris 1-2 µm along with some course (2-5 µm) particles. The fine debris particles are formed while fracturing of coarse debris during repeated sliding. The morphology of wear debris shows the presence of more TiO_2 particles removed during wear process it confirms the mechanism of wear is brittle and fragmentation of TiO_2 splats. In wear debris collected from TiO_2+10%SiC coating shows the similar kind of particles, the wear debris collected during sliding of coating generates less particles compared to other coating is show in fig-8c which sheared or rolled and agglomerated. The wear debris are very fine size 1-3 µm, Wear debris formed are compacted and smeared with worn surfaces for more polished are obtained. This may result high frictional area, lower contact stresses and hence lowest wear rate with lowest coefficient of friction compared to TiO_2 coating (Bajwa.S et al,2005).

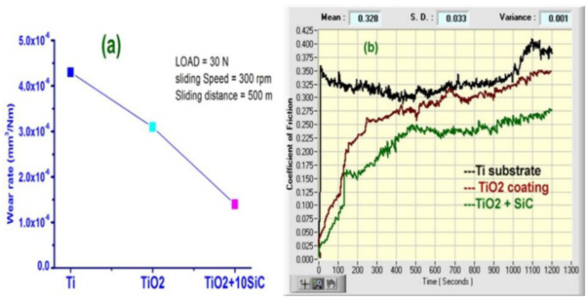

Fig-4 (a) Wear rate (b) Coefficient of friction

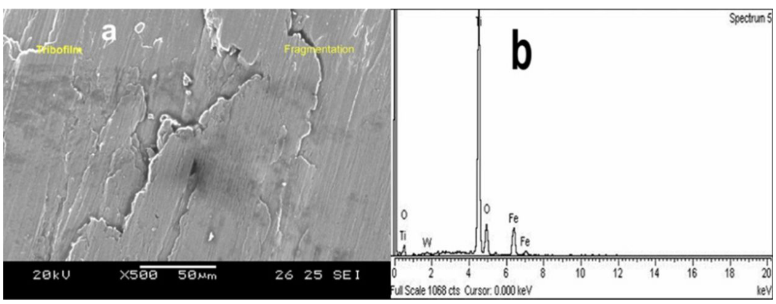

Fig-5 SEM Morphology of (a) Titanium worn surface (b) EDS analysis of Titanium worn surface

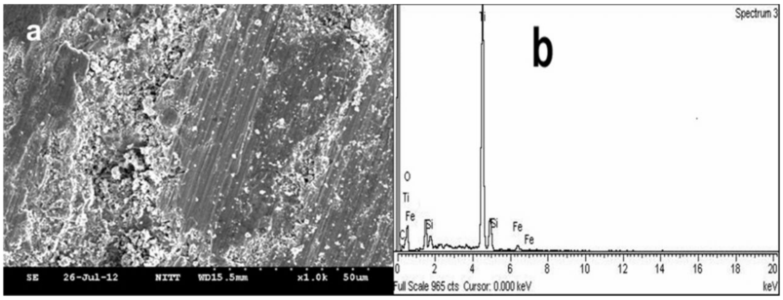

Fig-6 SEM Morphology of (a) TiO_2 worn surface (b) EDS analysis of TiO_2 worn surface

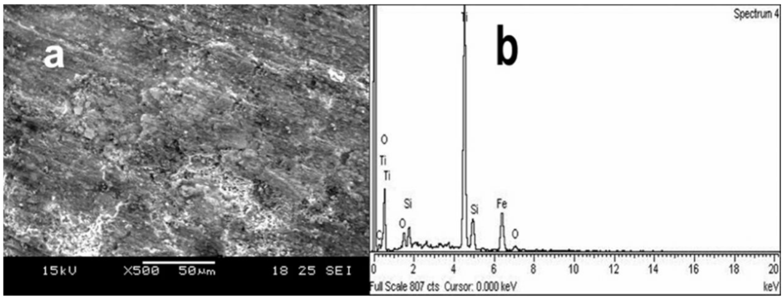

Fig-7 SEM Morphology of (a) TiO_2+10%SiC worn surface (b) EDS analysis of TiO_2+10%SiC coating

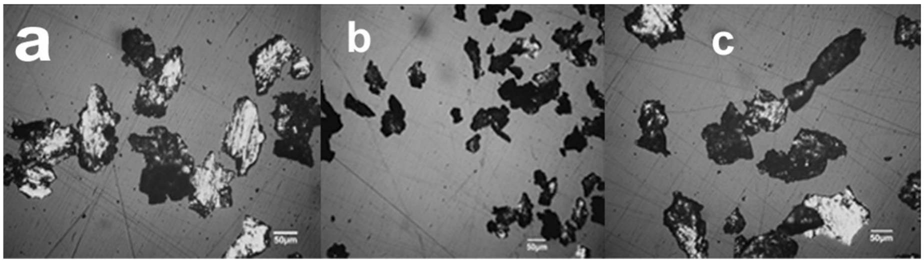

Fig -8 Wear debris of (a) Titanium, (b) TiO_2 coating and (c) TiO_2+10%SiC coating

4. CONCLUSIONS

1. Titania and SiC reinforced Titania coating was deposited by High Velocity Oxy Fuel spraying on Titanium substrate. The addition of SiC in TiO_2 coating matrix enhances the coating hardness.

2. Wear behavior of the Titanium, TiO_2 and TiO_2 + 10%SiC coatings were studied by Pin-on-disc machine as per ASTM G99-04 standard. Addition of SiC improves the wear resistance of TiO_2 coating. The worn surface morphology of the coatings were analysed by SEM and EDS.

3. The major wear mechanism of Titanium substrate is plastic deformation, fatigue and adhesive wear, whereas TiO_2 coating shows plastic deformation, fragmentation and brittle fracture as major wear mechanism.

4. Addition of SiC delays the wear transition from severe to mild wear and it forms tribolayer which prevents material removal and gives lower coefficient of friction. The mechanism of TiO_2 + 10%SiC coating is plastic deformation.

Acknowledgements

The authors wish to express sincere thanks to Dr.C.S.Ramachandran, Post Doctoral Fellow, State University of NewYark, U.S.A, for his technical support provided to carry out this investigation.

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